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Oxide etch process with high selectivity to nitride suitable for use on surfaces of uneven topography.

A plasma etch process is described for the etching of oxide (30) with a high selectivity to nitride, including nitride (20) formed on uneven surfaces of a substrate (2), e.g., on sidewalls of steps (10, 12) on an integrated circuit structure. The addition of one or more hydrogen-containing gases, preferably one or more hydrofluorocarbon gases, to one or more fluorine-substituted hydrocarbon etch gases and a scavenger for fluorine, in a plasma etch process for etching oxide in preference to nitride, results in a high selectivity to nitride which is preserved regardless of the topography of the nitride portions (22, 26) of the substrate surface. In a preferred embodiment, one or more oxygen-bearing gases are also added to reduce the overall rate of polymer deposition on the chamber surfaces and on the surfaces to be etched, which can otherwise reduce the etch rate and cause excessive polymer deposition on the chamber surfaces. The fluorine scavenger is prefer-

ably an electrically grounded silicon electrode associated with the plasma.

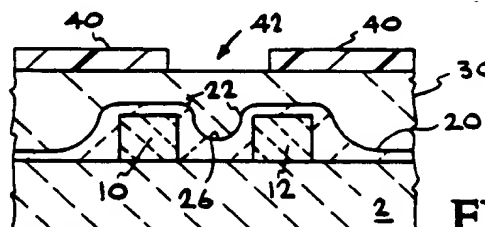


FIG. 1

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BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an oxide etch process which is highly selective to nitride. More particularly, this invention relates to an oxide etch process with high selectivity to nitride which can be used on surfaces of uneven topology.

2. Description of the Related Art

A significant challenge in semiconductor fabrication is to etch an oxide such as a silicon oxide, in the presence of a nitride, such as a silicon nitride, without also etching the nitride, i.e., while maintaining a high selectivity to the nitride. An example of such could be where an oxide layer to be etched is located over a nitride layer. Since both oxide and nitride materials generally etch at the same rate in a typical fluorocarbon chemistry etch plasma commonly used for etching oxide, a process of providing additional selectivity must be found.

When a fluorine-substituted hydrocarbon, such as C_3F_8 , is used as an etchant, the fluorocarbon radicals react in the plasma to form a passivating coating of a carbon-fluorine polymer which forms over the materials being etched, e.g., by exposed oxide and nitride surfaces on a substrate. However, this polymer is dissociated by oxide atoms formed during the etch of the exposed oxide portions. Thus, as the oxide, e.g., silicon oxide, continues to etch, the nitride portions etches at a much slower rate due to the presence of the passivating coating thereon. However, the passivating layer is also attacked by free fluorine atoms present in the plasma, and thus the nitride also continues to be etched. Thus, a selectivity over about 8:1 of silicon nitride to silicon oxide was not achievable with such prior art etch processes due to the presence of such free fluorine atoms in the plasma. Since for state of the art devices having submicron dimensions, i.e., VLSI and ULSI devices, selectivity of over 10:1 and even 30:1 are required, an etch process for etching oxide in preference to nitride with a selectivity of over 10:1 would be highly desirable.

In our parent application Serial No. 07/941,501, the subject matter of which is hereby incorporated by reference, we described and claimed the provision of a scavenger for fluorine such as a source of silicon or carbon. This scavenger for fluorine, when used in combination with such fluorine-substituted hydrocarbon etch gases, results in the formation of a carbon-rich polymer which does not dissociate over nitride surfaces, apparently due to either the reduced free fluorine content in the plasma, or the

reduced fluorine content in the polymer, or both. In any event, this use of a scavenger for fluorine in combination with fluorine-substituted hydrocarbon etch gases results in an oxide etch having a selectivity to nitride, i.e., a preference for oxide etching over nitride etching, of over 10:1, and up to as high as approaching infinity.

However, more recently an additional problem has been discovered where at least the nitride surfaces of the nitride/oxide structure being etched are not flat, as for example, the sidewalls of a slot or on raised steps such as, for example, nitride-coated polysilicon lines. This type of structure is illustrated in Figure 1 wherein raised polysilicon lines 10 and 12, formed over a substrate 2, are coated with a conformal layer 20 of nitride, over which is formed an oxide layer 30 and a photoresist mask 40.

When oxide layer 30 is etched, through mask opening 42 in photoresist mask 40, down to conformal nitride layer 20, nitride portions 22 on the sidewalls of raised polysilicon lines 10 and 12 are also at least partially etched, indicating that the above-described protective polymer is either not forming on such generally vertical surfaces (surfaces generally perpendicular to, or at least not planar with, the underlying substrate), or the protective polymer is being more readily attacked by the etchant gases on such nonplanar surfaces than the corresponding polymer portions formed on horizontal surfaces, i.e., surfaces generally planar to the underlying substrate, such as nitride portion 26 between raised lines 10 and 12.

It would, therefore, be desirable to provide an oxide etch process highly selective to nitride which is suitable for use on surfaces of uneven topography wherein nitride surfaces which are not planar to the underlying substrate, including sidewalls on slots or raised portions, will be resistant to etching by the oxide etch process.

SUMMARY OF THE INVENTION

The invention is defined in claims 1, 15 and 23, respectively. Particular embodiments of the invention are set out in the dependent claims.

We have found that the addition of one or more hydrogen-containing gases, preferably one or more hydrofluorocarbon gases, to one or more fluorine-substituted hydrocarbon etch gases and a scavenger for fluorine, in a plasma etch process for etching oxide in preference to nitride, results in a high selectivity to nitride which is preserved regardless of the topography of the nitride portions of the substrate surface. In a preferred embodiment, one or more oxygen-bearing gases are also added to reduce the overall rate of polymer deposition on the chamber surfaces and on the surfaces to be

etched, which polymer deposition can otherwise, respectively, reduce the etch rate, and cause excessive polymer deposition on the chamber surfaces.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a fragmentary vertical cross-sectional view of a typical structure to be etched by the process of the invention, having uneven topography with oxide portions to be etched and nitride portions which are generally perpendicular to the underlying substrate.

Figure 2 is a cross sectional view of a preferred etch apparatus suitable for use with the process of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The invention comprises an improved oxide plasma etching process having a high selectivity to nitride which is suitable for use with uneven topographies and comprises the addition of one or more hydrogen-bearing gases and the optional addition of one or more oxygen-bearing gases to an etchant gas comprising one or more fluorine-substituted hydrocarbon gases in contact with a scavenger for fluorine. The gases form a polymer on the surfaces to be etched, and the portion of this polymer which forms over nitride surfaces is apparently not decomposed as readily as the polymer formed in the etch process described in our parent application Serial No. 07/941,501.

a. Hydrogen-Bearing Gases

The one or more hydrogen-bearing gases, which are added to the one or more fluorine-substituted hydrocarbon etchant gases, may comprise hydrogen and/or one or more hydrogen-containing fluorocarbons. While the use of hydrogen (H_2) is within the scope of the invention, it is preferred that a less flammable source of hydrogen be used. In a preferred embodiment the one or more hydrogen-bearing gases consist essentially of one or more hydrofluorocarbon gases having the formula CH_xF_{4-x} , where x is 1-3. Most preferably the hydrogen-bearing gas consists essentially of monofluoromethane (CH_3F).

The amount of hydrogen-bearing gas or gases added to the one or more fluorine-substituted hydrocarbon etchant gases may range from as little as 1 volume percent (vol. %) to as high as 100 vol. % of the one or more fluorine-substituted hydrocarbon etchant gases. Preferably, the amount of hydrogen-bearing gas added to the fluorine-substituted hydrocarbon etchant gases will range from about 5 vol. % to about 30 vol. % of the fluorine-

substituted hydrocarbon etchant gases.

b. Oxygen-Bearing Gases

The one or more oxygen-bearing gases, which are optionally further added to the gaseous mixture to control the polymer formation during the etching process, may comprise solely oxygen (in the form of O_2 , O_3 , and mixtures of same) or an oxygen-bearing gas such as CO, CO_2 , or an oxide of nitrogen (N_xO_y , where x is 1 to 2 and y is 1 to 2), or mixtures of same with one another and/or with oxygen and/or ozone. Of such gases CO, CO_2 , and mixtures of same are preferred. The amount of such oxygen-bearing gas or gases may range from as little as 1 vol. % to as much as 300 vol. % of the one or more fluorine-substituted hydrocarbon etchant gases. Preferably, the oxygen-bearing gas will range from about 50 vol. % to about 200 vol. % of the fluorine-substituted hydrocarbon etchant gases.

c. Fluorine-Substituted Hydrocarbon Etchant Gases

The one or more fluorine-substituted hydrocarbon etchant gases used in the oxide plasma etch process of the invention include CF_4 , C_2F_6 , C_3F_8 gases, as well as mixtures of same, which do not contain hydrogen and generate only carbon ions and fluorine ions. The amount of such fluorine-substituted hydrocarbon etchant gas or gases which are flowed into an etch chamber of, for example, about 8-10 liters in volume, may range from about 1 standard cubic centimeters per minute (sccm) to about 100 sccm, and preferable from about 10 sccm to about 40 sccm. It will, however, be understood by those skilled in the art that such flow rates are relative to the etch chamber volume and should be adjusted upwardly or downwardly, as the case may be, for larger or smaller etch chambers.

d. Etch Process Temperature and Pressure Parameters

The temperature of the substrate being etched will be maintained within a range of from about $10^\circ C$ to about $110^\circ C$, and preferably will be maintained at from about $80^\circ C$ to about $100^\circ C$. Temperatures below about $10^\circ C$ are considered too low for practical operation of the etch process (since the substrate tends to heat up during the etch process), while temperatures in excess of $110^\circ C$ may damage other components present on the substrate, such as, for example, the photoresist mask.

The pressure in the etch chamber during the plasma etch process will range from about 0.013

Pa to about 13.3 Pa (0.1 milliTor to about 100 milliTor), and preferable from about 0.133 Pa to about 5.32 Pa (1 milliTor to about 40 milliTor).

e. Fluorine Scavenger

With respect to the need for the addition of a fluorine scavenger to the process of the invention, although the exact mechanism for the present process is not completely understood, and there is no intent to be bound by any particular theories of operation, generally when a fluorocarbon etch gas, such as CF_4 , C_2F_6 , C_3F_8 , and the like, that contains both carbon and fluorine, is exposed to a plasma, various fragments are generated in the plasma, including free fluorine atoms, CF , CF_2 , and CF_3 radicals and the like. The fluorine is available to etch silicon oxides on a substrate. However, during the course of the etch process, a polymer of carbon and fluorine is also formed, that deposits onto the substrate, i.e., over both oxide and nitride surfaces thereon, forming a passivating layer. The polymer may contain about 30% by weight of carbon and about 60% by weight of fluorine. Such polymers are attacked by oxygen atoms, and thus the oxygen atoms from the oxide layer will dissociate the polymer as it is formed, without interfering with the etch of the oxide. However, when no oxygen is present, such as when a non-oxygen-containing layer is reached, i.e., a nitride layer, the silicon oxide will continue to etch, but the passivated nitride layer will etch at a slower rate.

However, the passivating polymer may also be dissociated by fluorine, and the continual formation of fluorine ions and radicals in the plasma will bombard and other wise attack the polymer layer as well, causing the polymer to dissociate, whereupon the nitride layer will be etched as well by the plasma. Thus, the maximum selectivity of an oxide over nitride achieved prior to the process described in our parent application (Serial No. 07/941,501) was about 8:1.

However, we found that reducing the fluorine content of the passivating polymer, and reducing the amount of free fluorine in the plasma, reduces the dissociation of the passivating polymer. Thus, if a scavenger for fluorine, such as a source of silicon atoms or carbon atoms, is contacted with the plasma, silicon atoms or carbon atoms can combine with fluorine atoms, for example, to form SiF_x , thus reducing the number of free fluorine ions in the plasma. The polymer deposited onto the nitride layer thus may have less fluorine atoms or more carbon atoms and a "carbon-rich" polymer may result. A carbon-rich polymer is defined for the present purposes as a polymer that contains less than about 40% by weight of fluorine and over about 50% by weight of carbon and which is inert

to fluorine-containing plasma etchants. Thus, when a carbon-rich polymer is deposited onto a nitride layer, almost no decomposition or reaction of the carbon-rich polymer occurs, in turn providing an almost infinite selectivity for an oxide layer over a nitride.

A source of silicon can be provided in several ways; for example, a silicon-containing gas, such as, for example: silane (SiH_4); a substituted silane, such as diethyl silane ($\text{SiH}_2(\text{C}_2\text{H}_5)_2$), SiF_4 , and the like; and tetraethylorthosilicate (hereinafter TEOS) can be added to the plasma. The silicon-containing gas decomposes to form free silicon which will scavenge free fluorine atoms resulting in the formation of a carbon-rich carbon-fluorine polymer coating on the nitride layer which apparently is not attacked during the etch process resulting in a very high selectivity of the etch process to nitride.

Another method of forming such a carbon-rich carbon-fluorine polymer is by providing a source of solid elemental carbon or silicon, e.g., a silicon mesh or a non porous surface, in the plasma area where the carbon or silicon acts as another electrode. A preferred method of carrying this out is described in copending Collins et al. U.S. Patent Application Serial No. 07/941,507, filed September 8, 1992, and assigned to the assignee of this invention, the disclosure of which is hereby incorporated by reference. In that application, an RF powered plasma etch chamber is described containing a source of free silicon, which can be, for example, a third electrode made of silicon or other source of free silicon in contact with the plasma, such as a silicon liner in the chamber walls. The third electrode can also be made of graphite as a source of carbon atoms that can scavenge fluorine. Preferably, the temperature of such an auxiliary electrode is maintained within a range of from about 200°C to about 300°C . Providing a separate heated silicon source, as well as heated quartz sidewalls, in an etch reactor to promote formation of the desired carbon-fluorine polymer, is further discussed in Rice et al. U. S. Patent Application Serial No. _____ (Applied Materials Patent Docket 603), entitled "PLASMA ETCH APPARATUS WITH HEATED SCAVENGING SURFACES", mailed to the USPTO on October 15, 1993, and assigned to the assigned of this invention, and the disclosure of which is hereby incorporated by reference into this application.

f. Etch Plasma Parameters

The plasma generated during the oxide plasma etch process of the invention generally may comprise any plasma capable of being conventionally produced in a plasma chamber, or an adjacent chamber, for example, by providing a grounded

electrode and a second electrode connected to a source of RF power.

In a preferred embodiment, however, the plasma utilized with the oxide plasma etch process of the invention is a high density plasma which may be defined as an plasma generated by an electromagnetically coupled plasma generator, in contrast to a conventional capacitively coupled plasma generator. Various examples of such electromagnetically coupled plasma generators are described in copending Marks et al. U.S. Patent Application Serial No. 07/826,310, assigned to the assignee of this invention, and the disclosure of which is hereby incorporated by reference.

As stated in the above mentioned copending Marks et al. Serial No. 07/826,310, the term "electromagnetically coupled plasma generator" is intended to define any type of plasma generator which uses an electromagnetic field, rather than a capacitively coupled generator, to generate a plasma. Such electromagnetically coupled plasma generators can generate a plasma having an ion density of greater than about 10^{10} ions per cubic centimeter which is characterized herein as a "high density" plasma, which is the preferred plasma density for use in the process of the invention.

Included within the term "electromagnetically coupled plasma generator", for example, is an electron cyclotron resonance (ECR) type plasma generator such as described in Matsuo et al. U.S. Patent 4,401,054; Matsuo et al. U.S. Patent 4,492,620; and Ghanbari U.S. Patent 4,778,561 (cross-reference to which three patents is hereby made); as well as in an article by Machida et al. entitled "SiO₂ Planarization Technology With Biasing and Electron Cyclotron Resonance Plasma Deposition for Submicron Interconnections", published in the Journal of Vacuum Science Technology B, Vol. 4, No. 4, Jul/Aug 1986, at pp. 818-821.

Also included in the term "electromagnetically coupled plasma generator" for example, is an inductively coupled helical or cylindrical resonator such as described in Steinberg et al. U.S. Patent 4,368,092 or Flamm et al. U.S. Patent 4,918,031, cross-reference to both of which patents is hereby made.

Further included in the term "electromagnetically coupled plasma generator" for example, is a helicon diffusion resonator such as the plasma generator described in Boswell U.S. Patent 4,810,935, cross-reference to which is also made.

Ogle U.S. Patent 4,948,458, cross-reference to which is also hereby made, describes yet a further type of electromagnetically coupled plasma generator comprising a transformer coupled plasma generator.

The RF source power level of such a high density plasma may vary from about 500 watts to

about 5 kilowatts (kw), depending upon the particular type of plasma generator, size of chamber, desired etch rate, etc. For example, using an ECR type electromagnetically coupled plasma generator in association with a etch chamber of about 6 liters and a desired etch rate of about 5000 Angstroms per minute, the power would typically range from about 2 to about 3 kW. For an inductive type electromagnetically coupled plasma generator used in association with a 2 liter etch chamber and a desired etch rate of about 5000 Angstroms per minute, the power would typically range from about 1 to about 2 kW. When a high density plasma is to be generated the power density, i.e., the power level relative to the volume of the plasma generating chamber, should be equivalent to a power level of about 1000 Watts in a 4 liter plasma generating chamber. RF bias power is typically applied to the electrode on which the substrate being etched resides, using the chamber wall as the ground and/or using another electrode as ground. Bias power is adjusted to yield negative DC bias of several hundred volts on the substrate being etched. Typical bias power is 600-1400 Watts for a 200 millimeter diameter substrate to yield 100-300 volts DC bias.

g. Preferred Etch Apparatus

Figure 2 illustrates an etch apparatus suitable for use in the practice of the present oxide plasma etch process of the invention, wherein a reactor system 100 includes a vacuum chamber housing 110, formed of anodized aluminum or other suitable material, having sidewalls 120 and top and bottom walls 130 and 140 respectively. The top wall 130 has a central opening 150 between a lower chamber substrate processing section 160B defined between sidewalls 120-120 and an upper chamber plasma source section 160A defined by a dome comprising dome sidewalls 17W and a dome topwall 170T. The dome topwall 170T may be configured as an inverted single or double walled cup which is formed of a dielectric, such as quartz.

The evacuation of the interior of the chamber housing 110 (chamber 160) is controlled by a throttle valve 180 in a vacuum line 190 which is inserted in the bottom wall 140 and connects to a vacuum pumping system 210 comprising one or more vacuum pumps.

Process gases can be supplied to the chamber 110 by three manifold injection sources, G1, G2, and G3 located respectively at the base of the source region 160A, at the dome top 170T, and peripherally about the substrate 5 to be etched. The overall gas flow is along path 34 from the chamber source region 160A toward the substrate 5, and along path 36 from the substrate 5 to the outlet manifold 330, and along path 37 from the

outlet manifold 330 to the vacuum system 210.

RF energy is supplied to the dome adjacent dome sidewall 17W by a source comprising an antenna 300 of at least one turn or coil which is powered by an RF supply and matching network 310. The antenna 300 is tuned to resonance, or resonated using lumped elements, i.e., for example, capacitors, for efficient inductive coupling with the plasma source. A plasma is generated in the dome concentrated in the volume defined within the coil antenna 300. Active species, including ions, electrons, free radicals, and excited neutrals, move toward the substrate 5 to be etched by diffusion and by bulk flow due to the gas flow generated by the gas manifold system G1, G2, and G3. A bias energy input arrangement 410, comprising a source 420 and a bias matching network 430, couples RF energy to the substrate support electrode 320 for selectively increasing the plasma sheath voltage at the substrate, and thus selectively increasing the ion energy at the substrate.

In the illustrated embodiment, the chamber 110 further incorporates a unique, three-electrode arrangement which provides the fluorine scavenger associated with the plasma as described herein. The substrate support electrode 320 comprises a cathode, the chamber side walls 120 comprises the anode, and a third electrode comprises a sacrificial electrode 17S located beneath the dome top plate 170T. This third electrode may be floating, but is preferably either grounded or connected to a RF power supply 400 and is preferably made of silicon or a silicon-containing alloy, or carbon such as graphite. Excess fluorine ions then interact with this third electrode to form SiF_x or CF_x , as the case may be, thereby reducing the total number of fluorine ions in the plasma.

The following examples will serve to illustrate the various embodiments of the invention.

Example I

A 150 millimeter diameter substrate comprising a silicon wafer having a photoresist mask and a layer of silicon oxide beneath the mask of about 5000-10,000 Angstroms thick over a silicon nitride layer deposited by PECVD, and which, in turn was formed over steps on the silicon wafer, forming a structure similar to the one shown in Figure 1, was etched in an RF etch chamber as described above with respect to Figure 2, and commercially available from Applied Materials, Inc. as a Centura™ HDP Dielectric Etch System. A grounded third electrode made of silicon, and maintained in the etch chamber at a temperature of about 260°C, was used as the source of silicon comprising the fluorine scavenger. 20 sccm of C_3F_8 was flowed into the chamber as the fluorine-substituted hy-

drocarbon etching gas, together with 3 sccm of CH_3F as the hydrogen-bearing gas. The pressure in the etch chamber was maintained at about 0.4 Pa (3 milliTor) during the etch and the temperature of the substrate was maintained at about 100°C. The plasma generator power level was maintained at about 2000 watts. A bias voltage of minus 200 volts D.C. was maintained on the substrate during the etch by adjusting the RF bias power to 650 watts. The etch was carried out through the opening in the mask for about 2 minutes, thereby exposing the nitride layer beneath the etched opening in the oxide layer through the resist mask.

The respective oxide and nitride layers, including the portions of the nitride layer on the sidewalls of the steps, were examined by SEM and the ratio of etched oxide to etched nitride, i.e., the selectivity of the etch process of the invention to nitride on the flat regions was found to be about $\infty:1$, while the nitride to oxide selectivity on the sidewalls of the steps was found to be about 15:1.

Example II

To illustrate the process of Example I with the addition of an oxygen-bearing gas to the etch process of the invention, the procedure of Example I was repeated on a similarly coated substrate, except that 30 sccm of CO gas was also flowed into the chamber with the C_2F_6 fluorine-substituted hydrocarbon etch gas and the CH_3F hydrogen-bearing gas. The etch was again carried out for about 2 minutes. The respective layers were again examined by SEM, as in Example I, and the ratio of etched oxide to etched nitride, i.e., the selectivity of the etch process of the invention to nitride was again found to be about $\infty:1$ in the flat regions and over 12:1 on the nitride sidewalls. Substrates processed in accordance with Example II were further examined by SEM for any evidence of etch residues or polymer deposits on the substrates and no such materials were found, even after the processing of over 200 substrates in the etch chamber.

Thus, the process of the invention provides for the plasma etching of an oxide layer, in the presence of nitride, with a high selectivity to nitride which is independent of the position of the nitride layer with respect to the plane of the underlying substrate, by the addition of a hydrogen-bearing gas to a fluorine-substituted hydrocarbon etching gas used in connection with a fluorine scavenger. Furthermore, the etch rate may be increased, and the chamber wall deposits decreased, by the addition of an oxygen-bearing gas to the gas mixture during the etch process.

Claims

1. A process for plasma etching oxide in the presence of nitride capable of exhibiting high selectivity to nitride, including nitride on uneven surfaces, which comprises contacting said oxide with a mixture of gases comprising:
 - a) one or more fluorine-substituted hydrocarbon etching gases; and
 - b) one or more hydrogen-bearing gases; in the presence of a fluorine scavenger.
2. The process of claim 1, wherein the total amount of said one or more hydrogen-bearing gases ranges from about 1 vol.% to about 100 vol.% of said one or more fluorine-substituted hydrocarbon etching gases.
3. The process of claim 1 or 2, wherein said one or more fluorine-substituted hydrocarbon gases each have a formula $C_xF_{(2x+2)}$, where x is 1-3.
4. The process of claim 1 or 2, wherein said one or more hydrogen-bearing gases is selected from the group consisting of hydrogen, one or more hydrofluorocarbons having the formula $C_xH_yF_z$, and mixtures of two or more of same, where x is 1-3, y is from 1 to $2x+1$, and z is $2x+2-y$.
5. The process of claim 1 or 2, wherein said one or more hydrogen-bearing gases is selected from the group consisting of monofluoromethane (CH_3F), difluoromethane (CH_2F_2), trifluoromethane (CHF_3), and mixtures of two or more of same.
6. The process of claim 1 or 2, wherein said one or more hydrogen-bearing gases consists essentially of monofluoromethane (CH_3F).
7. The process of claim 2, wherein said mixture of gases further comprises one or more oxygen-bearing gases in an amount ranging from about 1 vol.% to about 300 vol.% of said one or more fluorine-substituted hydrocarbon etching gases.
8. The process of claim 7, wherein said one or more oxygen-bearing gases are selected from the group consisting of oxygen (O_2), ozone (O_3), carbon monoxide (CO), carbon dioxide (CO_2), an oxide of nitrogen (N_xO_y , where x is 1-2 and y is 1 to 2), and mixtures of two or more of same.
9. The process of claim 7, wherein said one or more oxygen-bearing gases are selected from the group consisting of carbon monoxide, carbon dioxide, and mixtures of same.
10. The process of claim 2, wherein said fluorine scavenger is selected from the group consisting of silicon and carbon.
11. The process of claim 10, wherein said fluorine scavenger is a silicon surface spaced from said oxide and nitride.
12. The process of claim 11, wherein said silicon surface fluorine scavenger is electrically associated with said plasma.
13. The process of claim 11, wherein said silicon surface fluorine scavenger is grounded.
14. The process of claim 11, wherein said silicon surface fluorine scavenger is maintained at a temperature within a range of from about 200 °C to about 280 °C.
15. An oxide plasma etch process capable of exhibiting high selectivity to nitride, including nitride sidewalls in an integrated circuit structure on a substrate, which comprises:
 - a) loading into an etch chamber a substrate containing an oxide layer and a nitride layer;
 - b) flowing into said etch chamber:
 - i) one or more fluorine-substituted hydrocarbon etching gases having the formula $C_xF_{(2x+2)}$, where x is 1-3;
 - ii) one or more hydrogen-bearing gases consisting essentially of hydrofluorocarbons having the formula $C_xH_yF_z$, where x is 1-3, y is from 1 to $2x+1$, and z is $2x+2-y$; and
 - iii) optionally one or more oxygen-bearing gases;
 - c) igniting a plasma in said chamber; and
 - d) contacting a fluorine scavenger with said plasma; whereby said oxide layer will be etched while maintaining a high selectivity to nitride.
16. The process of claim 15, wherein the total amount of said one or more hydrogen-bearing gases flowing into said chamber ranges from about 1 vol.% to about 100 vol.% of said one or more fluorine-substituted hydrocarbon etching gases.

17. The process of claim 15,
wherein the total amount of said one or more
hydrogen-bearing gases flowing into said
chamber ranges from about 5 vol.% to about
30 vol.% of said one or more fluorine-substi- 5
tuted hydrocarbon etching gases.
18. The process of claim 15,
wherein the total amount of said one or more
oxygen-bearing gases flowing into said cham- 10
ber ranges from about 0 vol.% to about 300
vol.% of said one or more fluorine-substituted
hydrocarbon etching gases.
19. The process of claim 15, 15
wherein said fluorine scavenger in contact with
said plasma comprises silicon.
20. The process of claim 15,
wherein said fluorine scavenger comprises sol- 20
id silicon in contact with said plasma.
21. The process of claim 20,
wherein said solid silicon fluorine scavenger is
electrically grounded. 25
22. The process of claim 19,
wherein said fluorine scavenger comprises a
silicon-containing gas in contact with said plas- 30
ma.
23. A process for plasma etching oxide in the
presence of nitride capable of exhibiting high
selectivity to nitride, including nitride on un-
even surfaces, which comprises contacting 35
said oxide with a mixture of gases comprising:
a) one or more fluorine-substituted hydro-
carbon etching gases;
b) one or more hydrogen-bearing gases;
and 40
c) optionally, one or more oxygen-bearing
gases;
in the presence of a fluorine scavenger com-
prising an electrically grounded silicon elec-
trode. 45

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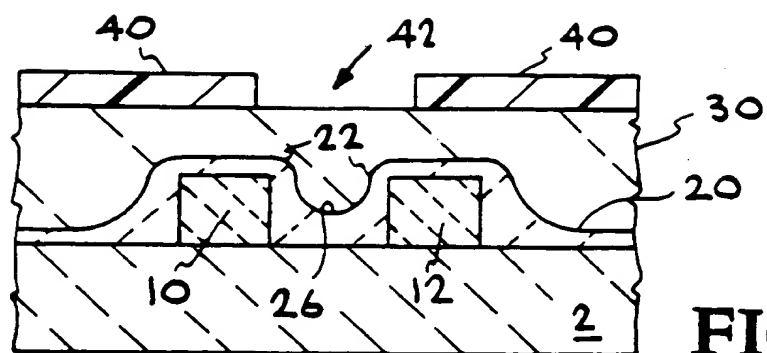


FIG. 1

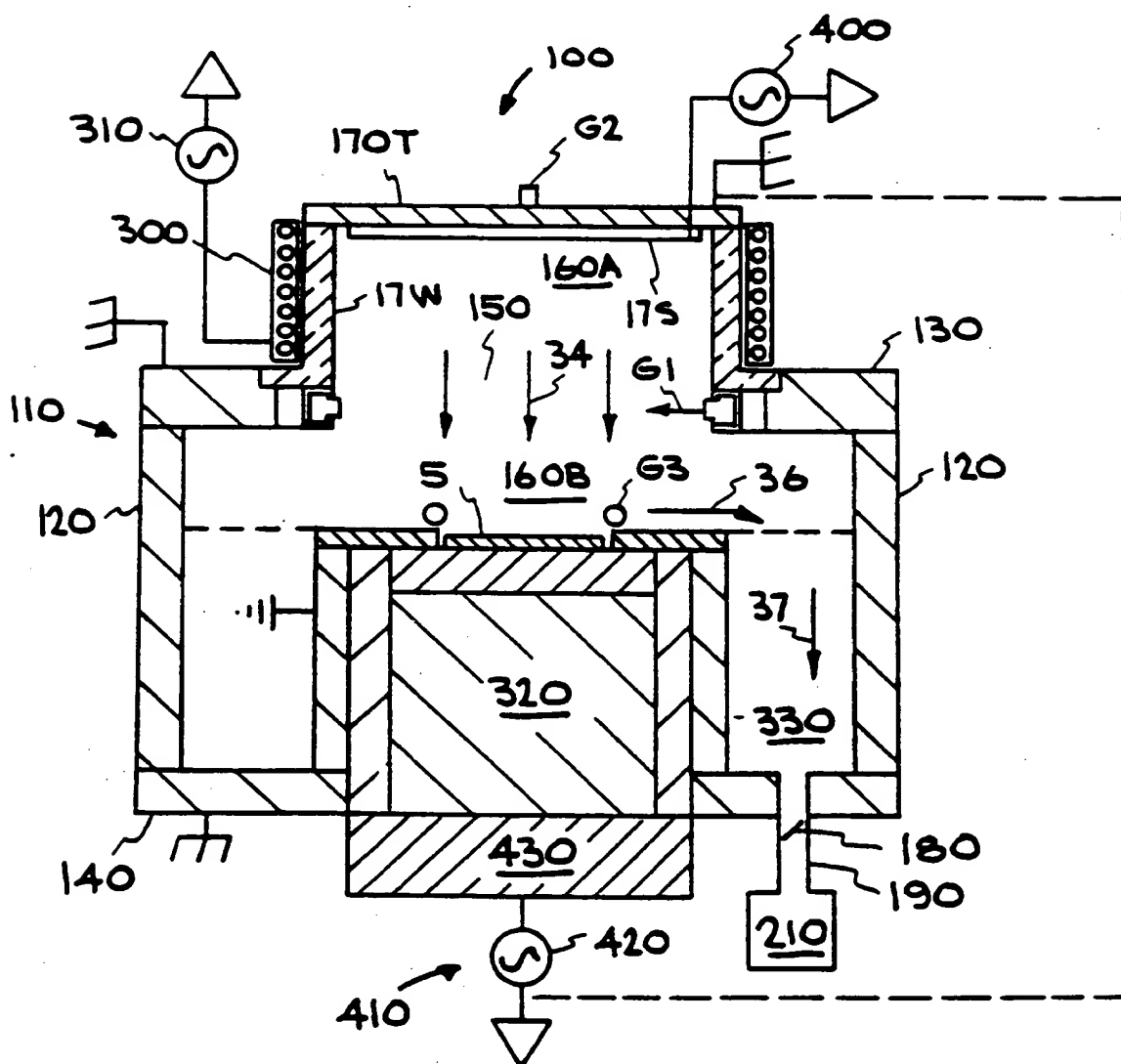


FIG. 2

(19)



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(54) Oxide etch process with high selectivity to nitride suitable for use on surfaces of uneven topography

(57) A plasma etch process is described for the etching of oxide (30) with a high selectivity to nitride, including nitride (20) formed on uneven surfaces of a substrate (2), e.g., on sidewalls of steps (10, 12) on an integrated circuit structure. The addition of one or more hydrogen-containing gases, preferably one or more hydrofluorocarbon gases, to one or more fluorine-substituted hydrocarbon etch gases and a scavenger for fluorine, in a plasma etch process for etching oxide in preference to nitride, results in a high selectivity to

nitride which is preserved regardless of the topography of the nitride portions (22, 26) of the substrate surface. In a preferred embodiment, one or more oxygen-bearing gases are also added to reduce the overall rate of polymer deposition on the chamber surfaces and on the surfaces to be etched, which can otherwise reduce the etch rate and cause excessive polymer deposition on the chamber surfaces. The fluorine scavenger is preferably an electrically grounded silicon electrode associated with the plasma.

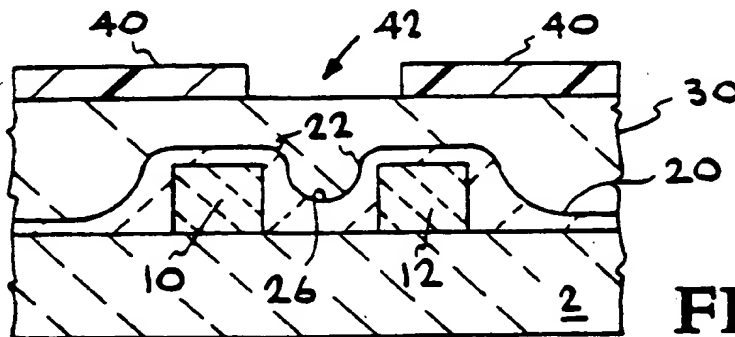


FIG. 1

EP 0 651 434 A3



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Application Number

which under Rule 45 of the European Patent Convention EP 94 11 7087 shall be considered, for the purposes of subsequent proceedings, as the European search report

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	MOSS AND LEDWITH: "The chemistry of the Semiconductor Industry" 1987, BLACKIE AND SON LTD., NEW YORK, USA XP002003419 * page 375 - page 378 *	1-3,23	H01L21/311
X	EXTENDED ABSTRACTS, vol. 93, no. 1, 21 May 1993, PRINCETON, NEW JERSEY US, pages 367-368, XP000430478 BECKER ET AL: "A method of obtaining high oxide to nitride selectivity in an MERIE reactor" * the whole document *	1-5, 15-18	
Y	EP-A-0 552 490 (APPLIED MATERIALS) 28 July 1993 * claims *	1-6, 10-13, 15-22	
		-/--	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			H01L
INCOMPLETE SEARCH			
<p>The Search Division considers that the present European patent application does not comply with the provisions of the European Patent Convention to such an extent that it is not possible to carry out a meaningful search into the state of the art on the basis of some of the claims</p> <p>Claims searched completely:</p> <p>Claims searched incompletely: 1-23</p> <p>Claims not searched:</p> <p>Reason for the limitation of the search:</p> <p>see sheet C</p>			
Place of search THE HAGUE		Date of completion of the search 21 May 1996	Examiner Gori, P
CATEGORY OF CITED DOCUMENTS		<p>T : theory or principle underlying the invention</p> <p>E : earlier patent document, but published on, or after the filing date</p> <p>D : document cited in the application</p> <p>L : document cited for other reasons</p> <p>& : member of the same patent family, corresponding document</p>	
<p>X : particularly relevant if taken alone</p> <p>Y : particularly relevant if combined with another document of the same category</p> <p>A : technological background</p> <p>O : non-written disclosure</p> <p>P : intermediate document</p>			

EPO FORM 1503 (01.91) (P0407)



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EP 94 11 7087

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
Y	IBM TECHNICAL DISCLOSURE BULLETIN, vol. 21, no. 10, March 1979, NEW YORK US, page 4016 XP002003416 BONDUR ET AL: "Gas mixing to prevent polymer formation during reactive ion etching" * the whole document *	1-6, 10-13, 15-22	
A	US-A-4 807 016 (TEXAS INSTRUMENTS) 21 February 1989 * column 2, line 17 - line 23 *	1,15,23	
A	JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY: PART A, vol. 3, no. 6, December 1985, NEW YORK US, pages 2627-2628, XP002003417 D'AGOSTINO: "Mechanisms of polymerization in discharges of fluorocarbons" * page 2627, right-hand column, line 4 - line 5 *	1,15,23	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	RESEARCH DISCLOSURE, no. 301, May 1989, HAVANT GB, page 340 XP002003418 ANONYMOUS: "Selective reactive ion etch for silicon oxide over silicon nitride" * the whole document *	1,15,23	

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EPO FORM 150 (01.92) (P0619)



European Patent
Office

PARTIAL EUROPEAN SEARCH REPORT

Application Number

EP 94 11 7087

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	<p>JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY: PART 8, vol. 7, no. 6, December 1989, NEW YORK US, pages 1352-1356, XP000249693 RILEY ET AL: "Comparision of etch rates of silicon nitride, silicon dioxide, and polycrystalline silicon upon O₂ dilution of CF₄ plasmas" * abstract *</p> <p>-----</p>	7-9,15, 18,23	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)

EPO FORM 150 (01/92) (PecClg)



EP 94117087.0 - C -

As indicated in US-A-4 807 016, col. 2, lines 17 to 23, and in J. of Vacuum Science and Technol., vol. 3, n° 6, page 2627, right-hand col., second paragraph, lines 1-2, some "fluorine-substituted hydrocarbons" (e.g. C₂F₄), "oxygen-bearing gases" (e.g. H₂O, CO, NO) or "hydrogen-bearing gases" (e.g. SiH₄, H₂O) are also considered as "fluorine scavengers". Consequently the meaning of these terms is not precisely limited in the relevant art and there exists a large overlapping in the definition of said terms. It follows that the scope of independent claims 1, 15 and 23 cannot be precisely determined, contrary to Art. 84 EPC.

According to Rule 45 EPC, the search has been carried out, for claims 1 to 23, in close connection with the description, while considering that :

- "fluorine-substituted hydrocarbon" is one or more of CF₄, C₂F₆, C₃F₈;
- "oxygen-bearing gas" is one or more of O_x, NO_x, CO_x;
- "hydrogen-bearing gas" is one or more of H₂, CH_xF_y;
- "fluorine scavenger" is unsubstituted or substituted silane, SiF₄, TEOS, solid silicon or carbon.



PATENT ABSTRACTS OF JAPAN

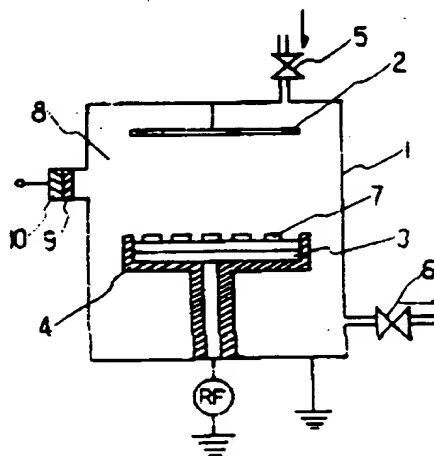
(11) Publication number: **57045927 A**(43) Date of publication of application: **16.03.82**

(51) Int. Cl

H01L 21/302(21) Application number: **55121564**(71) Applicant: **FUJITSU LTD**(22) Date of filing: **02.09.80**(72) Inventor: **INOUE MINORU****(54) VACUUM LEAKAGE DETECTOR FOR DRY ETCHING VACUUM CONTAINER****(57) Abstract:**

PURPOSE: To accurately and simply detect the vacuum leakage of a container by providing a window for passing a light to a vacuum container used for dry etching and a photodetector faced with the window and detecting the plasma light of N_2 or O_2 produced when its airtightness becomes improper.

CONSTITUTION: Opposite electrode 2 to become one electrode for generating a plasma is arranged in a vacuum container 1 forming a plasma etching device in such a manner that the potential of the electrode 2 is set to the same potential of the container 1. A water-cooled electrode 3 is arranged via a dielectric unit 4 for shielding from the container 1 oppositely to the electrode 2, a wafer 7 for a semiconductor device is placed as a member to be etched thereon, is energized by a high frequency power source, and the internal gas is converted to the plasma. In this configuration, a window 8 is opened at one side wall of the container 1, and a photodetector 10, e.g., a photodiode or the like is mounted via a filter 9 passing the characteristic wavelength of N_2 , O_2 thereat. In this manner, the plasma light of N_2 , O_2 always produced when the airtightness of the container 1 becomes improper is selectively detected, thereby effectively detecting the leakage.



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(19)



JAPANESE PATENT OFFICE

PATENT ABSTRACTS OF JAPAN

(11) Publication number: **62052714 A**

(43) Date of publication of application: **07.03.87**

(51) Int. Cl.

**G11B 5/66
G11B 5/704
G11B 5/72**

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KATO HIROYUKI
AZUMA TAKASHIRO**

(54) MAGNETIC RECORDING MEDIUM

(57) Abstract:

PURPOSE: To form a magnetic recording medium having excellent running stability and durability by forming a lubricative coating layer consisting of the cured matter of a specific fluoropolymer.

CONSTITUTION: The lubricative coating layer consisting of the cured matter of the fluoropolymer having a fluoroalkyl group and hydrolyzable functional group or silyl group having halogen atoms is provided on the front of a thin ferromagnetic film or the rear surface of a substrate after said thin film is provided as a magnetic layer on the substrate. The effect of a low friction characteristic and excellent corrosion resistance is developed by the fluoroalkyl group and the polymer is crosslinked and cured by the hydrolyzable

functional group or silyl group having halogen atoms, by which the toughness, wear resistance and the adhesiveness to the magnetic layer, etc. are improved. A protective layer may be provided of this polymer alone or in conjunction with other surface treating agents.

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